Adsorption Model for Off-Gas Separation

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SUMMARY

The absence of industrial scale nuclear fuel reprocessing in the U.S. has precluded the necessary driver for developing the advanced simulation capability now prevalent in so many other countries. Thus, it is essential to model complex series of unit operations to simulate, understand, and predict inherent transient behavior and feedback loops. The capability of accurately simulating the dynamic behavior of advanced fuel cycle separation processes will provide substantial cost savings and many technical benefits.

The specific fuel cycle separation process discussed in this report is the off-gas treatment system. The off-gas separation consists of a series of scrubbers and adsorption beds to capture constituents of interest. Dynamic models are being developed to simulate each unit operation involved, so each unit operation can be used as a stand-alone model or in series with multiple others.

Currently, an adsorption model has been developed in gPROMS software. Inputs include gas stream constituents, sorbent, and column properties, equilibrium and kinetic data, and inlet conditions. It models dispersed plug flow in a packed bed under non-isothermal and non-isobaric conditions for a multiple component gas stream. The simulation outputs component concentrations along the column length as a function of time from which the breakthrough data is obtained. Breakthrough data is an indication of the sorbent capacity by showing the length of time it takes to saturate the sorbent. It also outputs temperature along the column length as a function of time and pressure drop along the column length.

Experimental data will be input into the adsorption model to develop a model specific for iodine adsorption on silver mordenite as well as model(s) specific for krypton and xenon adsorption on various sorbents. The models will be validated with experimental breakthrough curves. The off-gas models will be made available via the server or web for evaluation by customers.

CONTENTS

FIGURES

ACRONYMS

gPROMS   general Process Modeling System

IPSC   Integrated Performance and Safety Codes

LDF   Linear Driving Force

NEAMS   Nuclear Energy Advanced Modeling and Simulation

PSE   Process Systems Enterprise

SafeSep   Safeguards and Separations

VBA   Visual Basic for Applications

SEPARATIONS AND WASTE FORMS
ADSORPTION MODEL FOR OFF-GAS SEPARATION

1.   INTRODUCTION

Modeling and simulations will aid in the future design of U.S. advanced reprocessing plants for the recovery and recycle of actinides in used nuclear fuel. The design of these processes must not only deliver high purity products but also minimize waste, proliferation risk, environmental impact, process complexity, and cost. The Nuclear Energy Advanced Modeling and Simulation (NEAMS) Program Safeguards and Separations (SafeSep) Integrated Performance and Safety Codes (IPSC) element is developing a dynamic plant level model which will allow simulations of separation processes for various configurations and operating conditions. This plant model will include the front end of the separations process (dissolution and potential voloxidation of the fuel), the separation processes, and the off-gas treatment system.

The reference case of unit operations for separation of off-gas consists of an interconnected series of adsorbers for the capture of tritium, Kr, Xe, and I, and scrubbers (absorbers) for the capture of C-14 and NOx as shown in Figure 1. Detailed off-gas modeling requirements were developed in FY 2010. These requirements for the off-gas modeling efforts include the model being dynamic, allowing for various unit operations to be incorporated for comparison and being flexible to allow for variation in unit operation sequencing and the components modeled. Also, each unit operation model will be able to be used as a stand-alone model or in series with other unit operation models.[1] Development of an adsorption model for off-gas treatment systems is the particular area of concern in the work described in this summary.

The objective of the modeling work presented herein was to solve the fundamental transport equations for adsorption in a packed bed in order to obtain a predictive unit operations model for separation of off-gas constituents. The stand-alone adsorption model will eventually be integrated with other unit operations models for use in a plant level model.
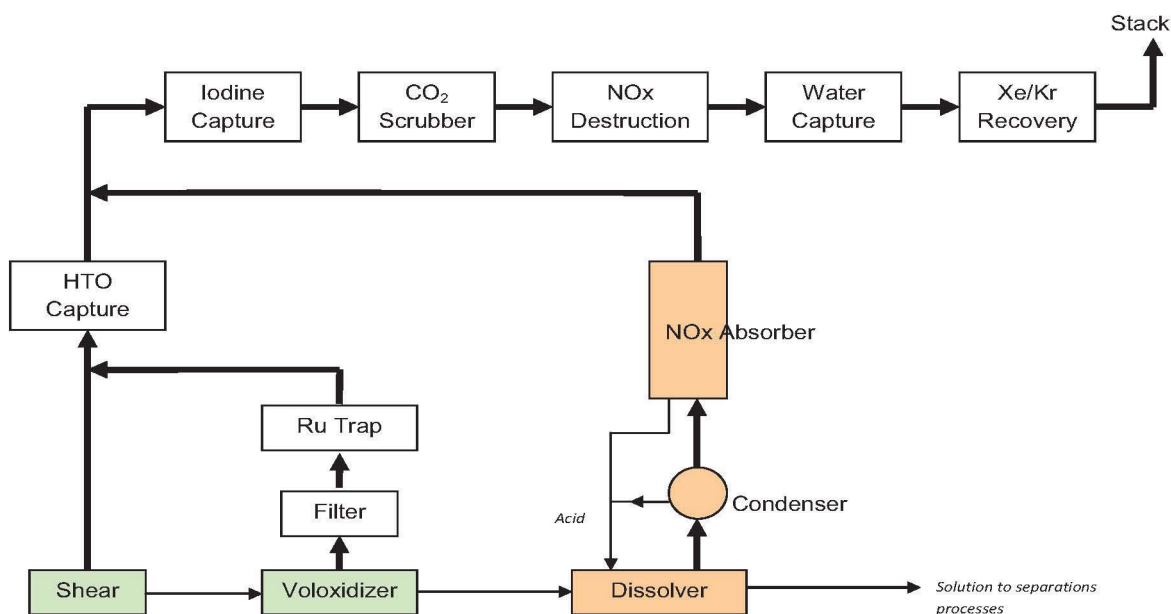

Figure 1: Schematic of example off-gas system.

2. MODELING PLATFORM

The off-gas models are being developed using general Process Modeling System (gPROMS) software. The gPROMS platform is an advanced process modeling environment available from Process System Enterprise (PSE). The gPROMS package comes with a library of models standard to the chemical process and modeling disciplines. These library models can be easily connected by unit and stream terms or by the topology interface (drag-and-drop method) to develop flow sheets. However, it is the platform for the construction and solution of custom model sets for which this architecture was really developed. Custom models can be developed via gPROMS code and linked together the same as the library models can be linked. The gPROMS platform is typically used for simulation, optimization, and parameter estimation.

The gPROMS package uses an equation oriented architecture supported by a suite of numerical solvers, and, therefore, is a very robust solver in which a simulation runs in a matter of seconds. Numerical algorithms used by gPROMS include, but are not limited to, finite difference, finite element, and various Gaussian quadrature techniques. The discretization method, order, and granularity of approximation can be specified by the modeler. The granularity can be either a uniform or non-uniform grid. The gPROMS package has a simple, user friendly programming language, efficient code diagnostics, efficiently manages discontinuities, and provides excellent customer support. This software interfaces with various other software packages through utilization of foreign objects. Examples of packages that gPROMS can be interfaced with are MS Excel, Matlab and Simulink, Fluent, and Aspen Plus.[2]

The gPROMS software has been used to model the adsorption bed discussed in this report and will also be used to create additional off-gas models. These off-gas models will all be interfaced with Excel, making use of the foreign objects feature in the software package. It is also planned to generate flow sheets of the off-gas system in gPROMS.

3. MATHEMATICAL MODEL

3.1 Assumptions

To develop a generalized model for the adsorption bed, the following assumptions for the off-gas separation process were made:

- Axially dispersed plug flow
- Ideal gas behavior
- No radial concentration gradient
- No radial temperature gradient
- Uniform voidage and particle size
- Thermal equilibrium
- Constant velocity

Due to low concentrations of the adsorbing species, large ratio of length to diameter of the column, and larger bed diameter than particle diameter, the assumptions listed above are reasonable.

3.2 Governing Equations

The mass balance describing the concentration gradient of adsorbing species along the adsorption column accounts for the rate of component uptake in the column, the axial dispersion, the convection term, and the rate of mass transfer into the particle. Based on the above assumptions, the mass balance for the adsorbing components is given by:

$$\frac{\partial C_i}{\partial t} = D_{zi}\frac{\partial^2 C_i}{\partial z^2} - v\frac{\partial C_i}{\partial z} - \frac{\rho_b}{\varepsilon}\frac{\partial q_i}{\partial t}; \ z \in (0, L) \tag{1}$$

where:

t = time, s
C_i = gas phase concentration of component i, mol/m^3
D_z = axial dispersion coefficient of component i, m^2/s
z = distance from the bed inlet in the axial direction, m
v = superficial gas velocity, m/s
ρ_b = bulk/bed density, kg/m^3
ε = overall bed void, dimensionless
q_i = solid phase concentration of component i, mol/kg
L = bed length, m

The rate of mass transfer into the particle, $\partial q_i / \partial t$, can be described by the linear driving force (LDF) equation:

$$\frac{\partial q_i}{\partial t} = k_i(q_i^* - q_i) \tag{2}$$

where:

q_i^* = equilibrium adsorption amount of component i, mol/kg
k_i = mass transfer coefficient of component i, s^{-1}

The solid phase equilibrium concentrations are represented by the extended Langmuir equation[3]:

$$q_i^* = \frac{q_{si}b_i(T)C_i}{1+\sum_{i=1}^{n}b_i(T)C_i} \tag{3}$$

$$b_i(T) = b_{i0}e^{-H_{ad,i}/(RT)} \tag{4}$$

where:

q_{si} = maximum concentration in the solid phase for component i, mol/kg
$b_i(T)$ = temperature dependent Langmuir equilibrium parameter of component i, m^3/mol
b_{i0} = Langmuir equilibrium constant for component i, m^3/mol
$H_{ad,i}$ = heat of adsorption of component i, J/mol
R = ideal gas constant, J/(mol*K)
T = temperature, K
n = number of components

The pressure distribution along the length of the packed bed is described by the Ergun equation[4]:

$$\frac{\partial P}{\partial z} = -K_D v - K_v v^2; \ z \in (0, L] \tag{5}$$

where:

P = pressure, bar
K_D = viscouse pressure loss term

K_v = kinetic pressure loss terms

For low Reynolds numbers (e.g. <5), the kinetic contribution to the total pressure loss is negligible, and the equation 5 reduces to Darcy's law[5].

For compressible flow, the energy balance for the packed bed is written as:

$$\left(C_{pg}\,\varepsilon\,\frac{P}{RT} + \rho_b C_{ps}\right)\frac{\partial T}{\partial t} = K_z\frac{\partial^2 T}{\partial z^2} - v\,\varepsilon\,C_{pg}\frac{P}{RT}\frac{\partial T}{\partial z} - \rho_b\sum_i\left(H_{ad,i}\frac{\partial q_i}{\partial t}\right) + \frac{4U_o}{d_c}\left(T - T_w\right); \; z \in (0, L) \quad (6)$$

where:

C_{pg} = gas phase heat capacity, J/(mol*K)
C_{ps} = solid phase heat capacity, J/(kg*K)
K_z = effective axial thermal conductivity, W/(m*K)
U_o = overall bed-wall heat transfer, W/(m^2*K)
d_c = column inner diameter, m
T_w = wall temperature, K

3.3   Initial and Boundary Conditions

Initial conditions (t = 0) for the adsorption process described by the governing equations are given by:

$$C_i = 0 \quad (7)$$

$$q_i = 0 \quad (8)$$

$$T = T_o \quad (9)$$

where:

T_o = initial bed temperature, reference temperature, K

The boundary conditions used to simulate the process are:

1. Inlet conditions (z = 0)

$$C_i = C_{in,i} \quad (10)$$

$$T = T_{g,in} \quad (11)$$

$$P = P_{in} \quad (12)$$

where:

$C_{in,i}$ = feed concentration of component i, mol/m^3
$T_{g,in}$ = feed gas stream temperature, K
P_{in} = feed gas pressure, bar

2. Outlet conditions (z = L)

$$\frac{\partial c_i}{\partial z} = 0 \tag{13}$$

$$\frac{\partial T}{\partial z} = 0 \tag{14}$$

The governing equations describing the adsorption process for off-gas separation along with the initial and boundary conditions were solved in the gPROMS modeling software. The spatial discretization method of backward finite difference method was utilized. A second-order solution parameter along with uniform grid spacing of 40 nodes was specified for convergence to the solution. This was found to give a converged solution in a few seconds and in which errors were minimized to less than 1%.

3.4 Evaluation of Model Parameters

The intraparticle mass transfer coefficient, k, in equation 2 is estimated using values for the effective diffusivity derived from experimental data according to the equation:

$$k_i = 60 \frac{D_{eff,i}}{(2r_p)^2} \tag{15}$$

where:

$D_{eff,i}$ = effective diffusivity of component i, m^2/s
r_p = sorbent particle radius, m

The axial distribution coefficient, D_{zi}, was calculated by the following set of semi-empirical correlations[6]:

$$D_{zi} = \frac{vL}{Pe_i} \tag{16}$$

$$\frac{1}{Pe_i} = \frac{\gamma_1 \varepsilon}{(Re_p)(Sc_i)} + \gamma_{2i} \tag{17}$$

$$Re_p = \frac{2r_p \rho_g v \, \varepsilon}{\mu_g} \tag{18}$$

$$Sc_i = \frac{\mu_g}{\rho_g D_{mi}} \tag{19}$$

$$\gamma_1 = 0.73 \tag{20}$$

$$\gamma_{2i} = 0.5 \left(1 + \frac{13 \gamma_1 \varepsilon}{(Re_p)(Sc_i)} \right)^{-1} \tag{21}$$

$$D_{mi} = \frac{10^{-5} T^{1.75} \left(1/M_i + 1/M_{cg} \right)^{1/2}}{P \left[(\Sigma V_{mi})^{1/3} + (\Sigma V_{mcg})^{1/3} \right]^2} \tag{22}$$

where:

Pe_i = Peclet number of component i, dimensionless
Re_p = Reynolds number, dimensionless
Sc_i = Schmidt number of component i, dimensionless
γ_1 = axial diffusion term, dimensionless
γ_{2i} = axial mixing term of component i, dimensionless
ρ_g = gas density, kg/m^3

μ_g = gas viscosity, Pa*s
D_{mi} = molecular diffusion of component i, m^2/s
M_i = molecular weight of component i, kg/mol
M_{cg} = molecular weight of carrier gas, kg/mol
ΣV_{mi} = molecular diffusion volume of component i, m^3/mol
ΣV_{mcg} = molecular diffusion volume of carrier gas, m^3/mol

The molecular diffusion volumes were calculated by adding the atomic diffusion volumes that were experimentally determined by Fuller, et. al. (1969).[6]

The Langmuir parameters q_{si}, maximum concentration adsorbed, and b_{i0}, the Langmuir equilibrium constant, are determined by fitting the single component Langmuir equation to the experimental adsorption isotherm of component i:

$$q_i^* = \frac{q_{si} b_i(T) c_i}{1 + b_i(T) c_i} \tag{23}$$

The values of the constants are regarded to be the same as those used for the extended Langmuir[7].

The viscous and kinetic pressure loss terms in the equation 5 are calculated by[4]:

$$K_D = 150 \frac{\mu_g (1-\varepsilon_b)^2}{\lambda_s^2 d_p^2 \varepsilon_b^3} \tag{24}$$

$$K_v = 1.75 \frac{(1-\varepsilon_b)\rho_g}{\lambda_s d_p \varepsilon_b^3} \tag{25}$$

where:

λ_s = shape factor of the sorbent particles
ε_b = bulk or bed void (packing), dimensionless
d_p = sorbent particle diameter, m

The effective bed conductivity, K_z, can be expressed as:

$$\frac{K_z}{k_g} = \frac{K_z^0}{k_g} + a(Pr)(Re_p) \tag{26}$$

$$Pr = \frac{\mu_g C_{pg}}{k_g} \tag{27}$$

where:

K_z^0 = static effective thermal conductivity, W/(m*K)
a = constant, dimensionless
k_g = gas phase thermal conductivity, W/(m*K)
Pr = Prandlt number, dimensionless

The value for the constant a equals 0.5 and the static effective conductivity accounts for the effects of conduction and radiation. At temperatures of less than 753 K, the radiative contribution to heat transport is small and therefore, negligible. The equation for the static effective conductivity, while neglecting radiative heat transfer is[5]:

$$\frac{K_z^0}{k_g} = \varepsilon_b + \frac{\beta_1(1-\varepsilon_b)}{\phi + \gamma \frac{k_g}{k_s}} \tag{28}$$

where:

k_s = solid phase thermal conductivity, W/(m*K)
β_1 = ratio of effective length between particle centers to the particle diameter, dimensionless

ϕ = ratio of effective thickness of fluid film adhering to solid to particle diameter, dimensionless
γ = ratio of effective length of solid relating to conduction to particle diameter, dimensionless

The wall-bed heat transfer coefficient, U_o, for cylindrical packing is given by[5]:

$$\frac{U_o d_c}{k_g} = 1.26 Re_p^{0.95} e^{-6 d_p/d_c} \tag{29}$$

4. RESULTS AND DISCUSSION

4.1 Current Adsorption Model

The separation of off-gas constituents modeled by the equations previously described is a multiple component model that describes the component concentration, gas stream composition and temperature along the column as a function of time and pressure drop across the bed. It is set up to distinguish between inert/carrier gas and adsorbing species involved in the process to obtain the entire gas composition. The model allows for a wide range of user inputs and can easily be scaled up to be used for systems larger than a bench scale model. The number of components can be increased and decreased, a wide range of parameter dimensions will be accepted, i.e. column height, various adsorbent properties can be specified, and a range of temperatures and velocities can be used.

Development of a user-friendly interface in Excel has been started so that users unfamiliar with the gPROMS software can easily specify the parameters for the desired off-gas system and run a simulation. Inputs for the model, which are user specified, include the bed void, sorbent parameters, column specifications, velocity, initial composition, initial temperature, initial pressure, component physical properties, and equilibrium and kinetic parameters. All of these parameters can be specified in the excel interface. Figure 2 shows the user input page of the interface.

Parameter	Value	Component Specifications			
Void	0.25	Number of components	3		
Superficial velocity (m/s)	0.0716	Adsorbing Species	I_2	CH_3I	
sorbent diameter (m)	0.0159	Inert Species	N_2		
mass of sorbent (kg)	0.01061				
bed length (m)	0.0381	All Species	I2	CH3I	N2
bed inner diameter (m)	0.0189	molecular weight (kg/mol)	0.127	0.142	0.028
Feed Temperature (K)	423	Feed concentrations (mol/m³)	9.59E-04	9.59E-04	28.79
Wall Temperature (K)	423	Deff	8.00E-06	7.00E-06	
Feed Pressure (bar)	1.01325	Qmax	0.951	0.96	
Simulation Time (s)	1000000	Keqo	1000	1000	

Figure 2: The input page of the user-friendly interface in Excel.

The simulation can be run from gPROMS, or, with a gORUN license, the simulation can be run directly from Excel. The capability of running the simulation directly from Excel will make it so that the user never has to directly interact with the gPROMS program. Figure 3 shows the simplicity of running the simulation from Excel using Visual Basic for Applications (VBA) coded solve button in the interface. The interface also has the ability to be stopped during a simulation through use of the stop button.

Sampling time   1000 s

Solve   Stop

Figure 3: VBA coded buttons in the Excel interface for running a simulation.

Outputs from the simulation include pressure along the bed length, temperature and component concentration along the column as a function of time, outlet composition, and the number of bed volumes processed. These results are generated in tabular form directly into the Excel interface. Breakthrough curves, temperature profiles and pressure drop curves are graphed automatically. Figure 4 shows an example of a breakthrough curve output from a simulation run using the Excel interface.
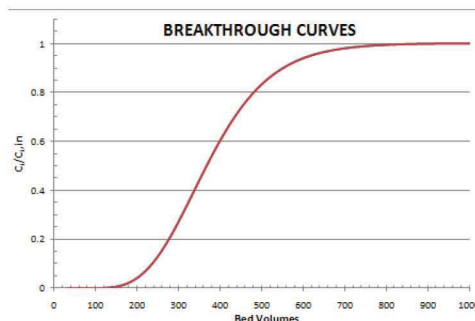
Figure 4: Graph generated in Excel interface.

4.2   Future Adsorption Model Work

Currently, the adsorption model has been developed using parameters determined for an iodine capture system. However, some of the parameters have been input as placeholder numbers to expedite the development of the generic adsorption model until correlations, known values, or experimentally determined parameters are used. Parameters that must be experimentally determined are the maximum concentration adsorbed and the equilibrium constant used in equations 3 and 23, and the effective diffusivity used to calculate the mass transfer coefficient (equation 15).

Once determined, the parameters will be input to generate a model specifically for the adsorption of iodine on silver mordenite. Data obtained from performing breakthrough experiments for the adsorption of iodine on silver mordenite at multiple initial concentrations, while keeping the feed velocity constant, will be used to generate an equilibrium isotherm[8]. The maximum concentration adsorbed will be determined from the asymptote where the slope of the isotherm approaches zero. The Langmuir equation will then be fit to the experimental isotherm by adjusting the Langmuir equilibrium constant. Thin bed kinetic experiments for iodine adsorption on silver mordenite, performed at Oak Ridge National Laboratory, will be used to determine effective diffusivities. Equilibrium and kinetic data of the same type will also be required to generate krypton and xenon specific models.

Additional currently unknown parameters for the iodine specific model are gas phase viscosity, gas and solid phase heat capacities, gas and solid phase thermal conductivities, and heat of adsorption. These parameters will be defined by either reported known values or correlations. Another option is to use a parameter estimation technique available in certain modeling software. As more becomes known about iodine adsorption on silver mordenite, competing species will be added to the model, reactions affecting the sorption process will be added, and silver mordenite aging will be accounted for.

The next step will be to validate the model by comparing simulation predictions to experimental breakthrough curves. The model will also be evaluated using other equilibrium models and kinetic correlations. This will aid in determining whether the Langmuir equilibrium model and LDF mass transfer assumptions are the best choice for the adsorption process. The user-friendly interface will be expanded to include other user defined inputs as model development continues and as need arises.

5.   CONCLUSIONS

In summary, a model has been developed to be used as the framework for the reference case unit operation used for capture of iodine, krypton, and xenon off-gas constituents. This generic model has been created for adsorption in a packed bed column with dispersed plug flow. It has the versatility to be used for multiple component systems, including both adsorbing and inert/carrier gas species and has the capability to accept a wide range of inputs. A user-friendly interface has been created in which the user can input system specific parameters and receive the output without having to navigate the modeling software.

The adsorption model is currently being used as a stand-alone model but will also be able to be used in series with other unit operation models. As this model is further developed, it will be made available for evaluation by the Sigma Off-gas Team and other customers.

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